No. 17.—X-RAY ANALYSIS (BY THE POWDER METHOD) AND MICROSCOPIC EXAMINATION OF THE PRODUCTS OF WEATHERING OF THE GINGIN UPPER GREENSAND.

By W. F. Cole.

Read 10th June, 1941 ; Published 17th August, 1942.

INTRODUCTION.

Available geological literature has revealed to the author a scarcity of published data on the weathering products of glauconite or glauconitic greensand. It was first proposed by Glinka (1) that with the loss of lime, potash, magnesia and ferric iron, glauconite was replaced by ferruginous clay. Cayeux (2) was however of the opinion that it alters to limonite. In recent years Denison, Fry and Gile (3) have shown that muscovite and biotite when undergoing weathering in the soil, pass by continuous variations from true micas through stages corresponding to glauconite and illite in composition. The weathering of the micas was accompanied by an increase in water content, decrease in K, and increase in Al at the expense of Fe and Mg. Chemical analyses showed that the final product of alteration of both micas was of about the composition of kaolinite.

In the present study an attempt has been made to identify, by means of the X-ray diffraction method of powder analysis, the weathering products of the upper greensand of Cretaceous age at Gingin, Western Australia (latitude 31° 21′ S., longitude 115° 54′ E.). This method of analysis is briefly described in an earlier paper (4). The microscopic examination was undertaken with the object of determining to what extent the optical properties were consistent with the X-ray conclusions. This work is preliminary to an investigation of the clay content and derivation of copper deficient soils of the Gingin district.

MATERIALS.

Location.—At Gingin, the Cretaceous rocks have the following sequence in descending order :—

1. The Upper Greensand or glauconitic sandstone which contains phosphatic nodules at its base.

2. The Chalk.

3. The Lower Greensand or glauconitic sandstone.

The distribution of these rock types is shown in Fig. 1 (5). The beds are practically horizontal. It is believed that the intermediate chalk is in the form of a lens which thins out to the north and south.

The topography of the country around Gingin is strongly undulating with a number of prominent hills rising above the level of Gingin Brook which immediately west of the town is about 270 feet above sea level. The heights of these hills are : Poison Hill, 724 feet ; Moorgup, 667 feet ; Ginginup, 666 feet ; One Tree Hill, 515 feet and Molecap, 510 feet (6).

Combining the geology and topography it is apparent that the upper greensand will outcrop on the highest hills and the lower hills will be formed from the underlying chalk and lower greensand. Hence in order to obtain specimens of the upper greensand and its overlying soil, a number of localities
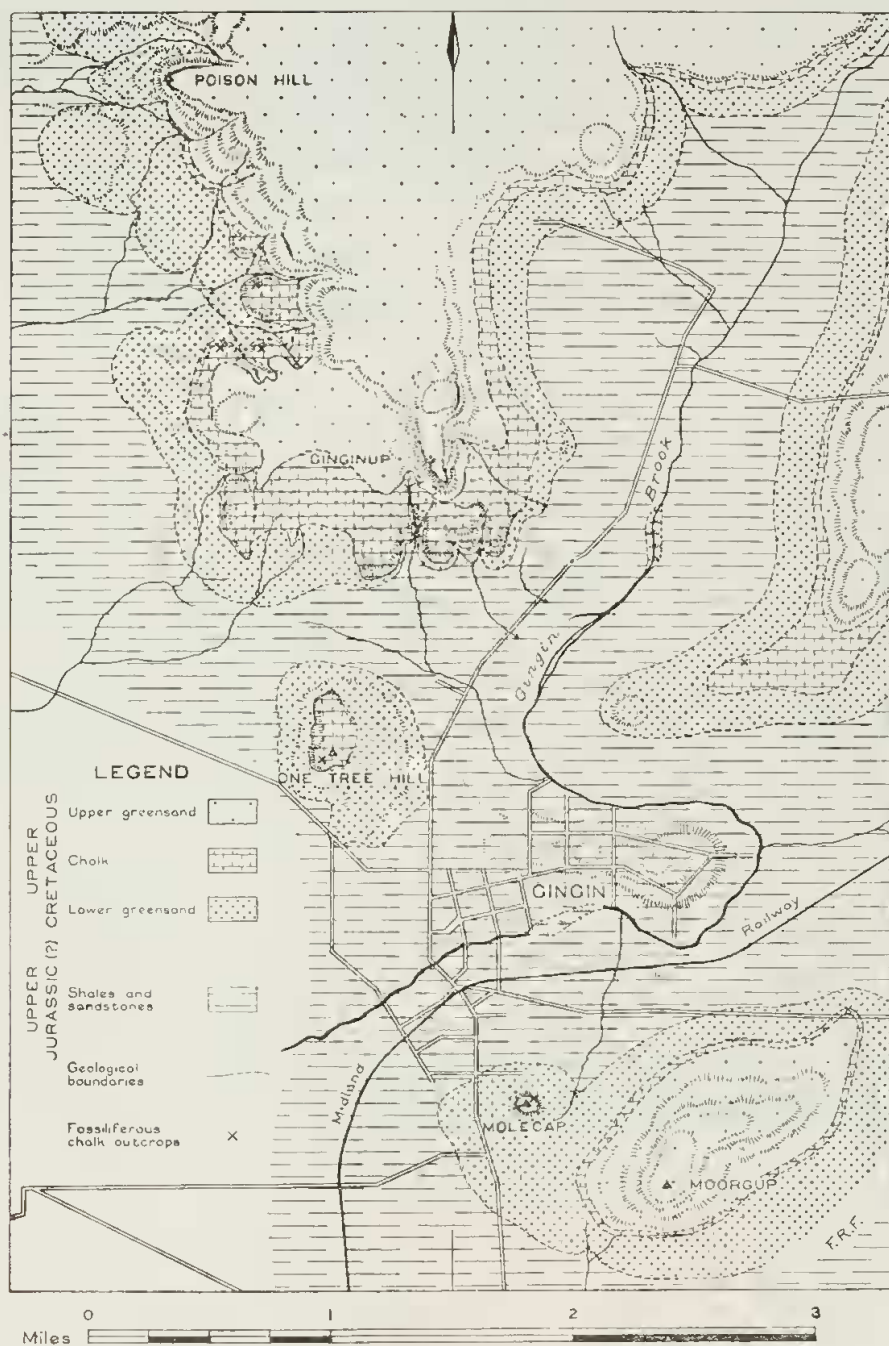
Figure 1.
Geological sketch map of Gingin. Drawn by F. R. Feldtmann and reproduced
from "Junior Geology."

were possible but Poison Hill was selected because it is the highest point in the district and thus offers least chance of contamination of the covering soil. Moreover a landslide on the southern slopes of the hill provided a vertical section from which three samples representing (1) soil, (2) subsoil and (3) upper greensand could be taken in the same profile (Fig. 2). Because the various soil horizons are clearly differentiated it is believed that the landslide has not affected the main body of the hill, and that natural contamination is negligible. X-ray evidence indicates a zoning of minerals to be expected from weathering in situ. Artificial contamination would therefore appear to be also negligible.

Professor E. de C. Clarke and Dr. D. Carroll of the Department of Geology of the University of Western Australia supervised the collecting of the samples.
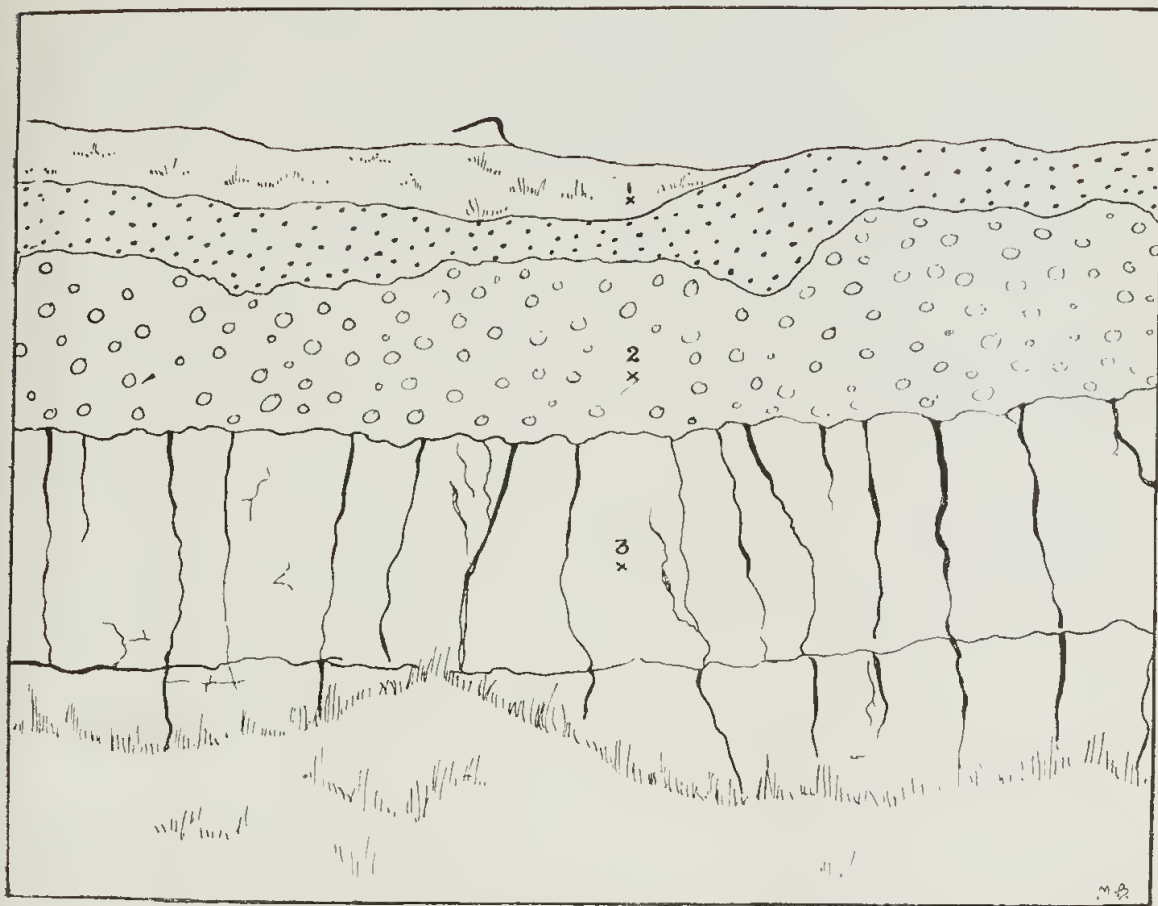
Figure 2.

Sketch of the landslide at Poison Hill, Gingin, from which the three samples representing (1) soil, (2) subsoil, and (3) upper greensand were taken in the same profile. Sample (1) was collected on the surface a little back from the edge of the landslip. The greensand carries vertical joints along which there is secondary deposit and at its base there is a line of ferruginous nodules (about four feet from the top of the greensand bed). The lower portion of the subsoil horizon, close to the greensand contact, contains much weathered greensand.
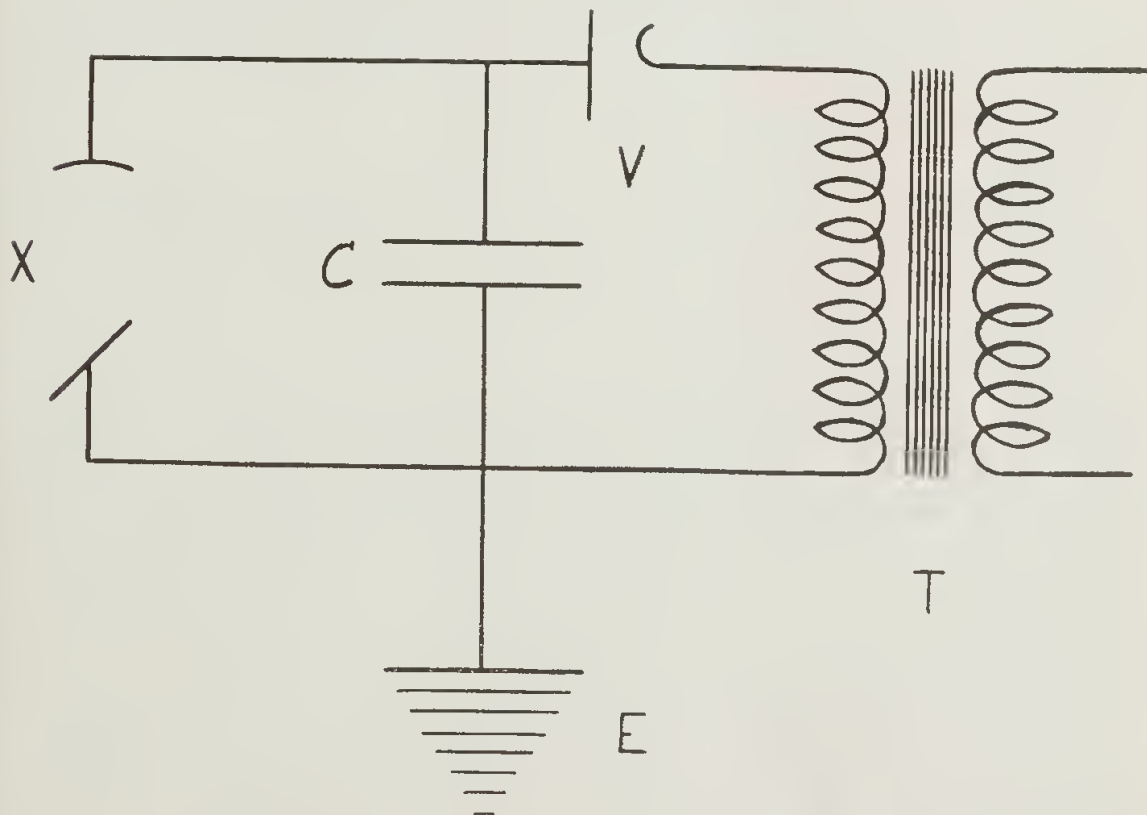

Figure 3.

Diagrammatic arrangement of the high tension unit. X-ray tube (X), Condenser (C), High Tension Valve (V), High Tension Transformer (T), Earth (E).

Method of Separation.—In the preparation of the material for X-ray analysis a number of grades of particle size were separated from each sample, but only two, a coarse fraction of particle size 61 μ and less and a fine fraction of particle size 2 μ and less, were examined.

The coarse fractions were obtained by sieving the three samples through a 250-mesh Tyler standard sieve of screen opening 0·061 mm.

The fine fractions were obtained by elutriation and settling. In the elutriation an Andrews Kinetic Elutriator was used to disperse the particles. Material of particle size 61 μ and less, obtained by sieving, was fed into the elutriator together with the washings off that material which did not pass through the 250-mesh sieve. The run off from the elutriator which carried particles of size 10 μ and less was collected in cylinders and the particles allowed to settle. Depending upon the mean temperature of the laboratory, the settling time was adjusted so that particles of effective diameter 2 μ and less, would fall a distance of 28 cms. At the end of the appropriate time the top 28 cm. was siphoned off and the clay particles removed from suspension by flocculation with calcium chloride, filtration, washing with absolute alcohol and air drying. No attempt was made to remove the organic matter present.

The coarse fractions of the soil, subsoil and greensand were dark brown brown and dark green in colour, whereas in the same order the fine fractions were chocolate brown, light brown and light green.

The amount of clay material collected in this manner was small. This, however, is in keeping with the mechanical analyses of soils overlying the Gingin greensand published by Hosking and Greaves (7). They note that the Wakea sand, which covers both the upper and lower ferruginous sandstones and grits from which it is formed in situ, rarely contains more than 10 per cent. clay.

EXPERIMENTAL DETAILS.

A Hilger-Mueller improved X-ray goniometer spectrograph was used with certain modifications previously referred to (4). Radiation was supplied by a Hilger all-steel water cooled gas X-ray tube. The tube was energised by a high tension unit arranged as in Fig. 3. This unit was modified from a Watson 200 K.V. Constant Potential Deep Therapy set.

Photographs were taken with both Fe and Cu radiation. It was found that films taken with Cu radiation showed a pronounced general scattering which was greatly improved by the use of Fe radiation. This can be explained by the facts that the samples contain minerals of high iron content and that Cu characteristic radiation is capable of exciting Fe characteristic radiation.

The Fe radiation was rendered monochromatic by the use of a manganese filter which served as a window for the X-ray tube. The action of such a filter is to suppress the K β radiation and transmit Kα radiation. The advantage of using filtered radiation was realized early in the work when. in examining a film of the greensand (61 μ and less) taken with Fe radiation, it was found that many lines in the central region could be possibly contributed to by the K β component. The manganese was electro-deposited on aluminium foil of thickness 25 μ. The method of preparation used is described by Wood (8). With the filter used in the course of this work no trace of the K β component appeared even after the longest exposures.

Suitable photographs with Fe Kα were obtained after 16 hours exposure with 4–5 mA tube current at 45–50 K.V. Films with unfiltered Cu radiation could be obtained with shorter exposures. When Cu radiation was used the manganese foil was still retained as a window for the X-ray tube.

For other experimental details regarding mounting of powders, films, etc., reference may be made to a previous publication (4).

ACCURACY OF RESULTS.

In this work the determination of d/n by a graphical method previously described (4) was not resorted to. The interplanar spacings were determined by a direct calculation from the Bragg equation $n\lambda = 2d \sin \theta$. This was rendered possible because quartz present in the coarse fraction of each sample produced characteristic blotchy lines which could easily be recognised and used for calibration. The blotchy character of the lines was associated with the particle size. It was found that r (the radius of curvature of the film) was constant along a film but varied from film to film. This variation was small and its extreme range was not more than $0 \cdot 5$ per cent.

Accuracy of Results for the Coarse Fractions.—Values of r calculated on the basis of the three quartz lines of interplanar spacing $3 \cdot 34$, $1 \cdot 814$ and $1 \cdot 538$ A were found not to vary by more than $0 \cdot 25$ per cent. Such a variation lies within the limits imposed by inability to measure any $2s$ (the separation of corresponding diffraction lines along the film in the equatorial plane) to any greater accuracy than $0 \cdot 1$ mm. Due then to an error in $2s$ of $0 \cdot 1$ mm. in lines used for calibration an error of $0 \cdot 25$ per cent. and $0 \cdot 09$ per cent. is possible for any value of d/n calculated over the range 10 A to 1 A.

On the assumption that there is no error in r involved in calibration measurements and that r is uniform across the film, the error in d n associated with an error of $0 \cdot 1$ mm. in $2s$ over the range from 10 A to 1 A varies from $1 \cdot 17$ per cent. to $0 \cdot 075$ per cent.

Hence the total maximum percentage error, assuming (a) uniform radius along a film and (b) d($2s$) $0 \cdot 1$ mm. in calibration and in measurement of an unknown line, is $1 \cdot 42$ per cent. to $0 \cdot 16$ per cent. over the range 10 A to 1 A. Weak lines may have a greater percentage error.

On this basis the maximum possible error in d/n at $2 \cdot 5$ A becomes $0 \cdot 01$ A so that for smaller spacings than this, d/n is recorded to $0 \cdot 001$ A.

Accuracy of Results for the Fine Fractions.—In the films of the fine fractions the absence of blotchy lines rendered the certain recognition of quartz impossible. Consequently, as no lines were available for calibration purposes, it was necessary to assume a constant radius of curvature for all films. The figure adopted was $2 \cdot 798$ cms.

In the absence of glauconite a line appearing with interplanar spacing $3 \cdot 34$ A is considered due to quartz. From an examination of Table I. it is seen that the maximum variation in d n for this line in the patterns of the fine fractions is $0 \cdot 01$ A. This is due to variations in $2s$ of $0 \cdot 01$ mm., corresponding to the maximum error considered possible in measurements of $2s$ for all but the very faintest lines. Hence, on this basis, it is considered that the assumption of a constant radius of 2.798 cms. yields results for the finer fractions which are no less inaccurate than those for the coarser fractions.

X-RAY DATA.

In Table I. are tabulated all observed values of d n for the samples examined. This includes the patterns obtained for samples which were heated in an electric furnace in air to 500°C. for 48 hours.

It has been previously pointed out (4) and (9) that the commonly occurring minerals in soil colloids include the clay minerals, quartz, and the oxides and hydroxides of Al and of Fe.

TABLE I.—INTERPLANAR SPACINGS OF THREE SAMPLES AND ASSIGNED ORIGINS. (UPPER FILTERED Fe

Upper Greensand.									Subsoil.					
61 μ and less.			2 μ and less.						61 μ and less.					
Possible Origin.	Unheated.		Possible Origin.	Unheated.		Possible Origin.	Heated 500°C.		Possible Origin.	Unheated.		Possible Origin.	Heated 500°C.	
	I.	d.u.		I.	d/n.		I.	d/n.		I.	d/n.		I.	d/n.
(M)	?	?	(M)	?	13·95	....	....	... .	M	ms	15·6*	....	....	....
G	s	10·12*	G	?	9·43	G(M)	s	10·12	G	vw	9·56*	U	?	12·75
U	w	5·43	..	....	....	....	....	....	K	vw	7·20	GM	m	10·02
G	m	4·94	....	vw	4·99	....	....	....	U	vw	5·47	....	....	....
G(M)		4·50	G(M)	s	4·48	G(M)	m	4·45	GM	vw	4·93	....	....	....
QGo	s {	4·26							GM	ms {	4·53	GM	w-m	4·47
Cg		4·09†	Cg	m(d)	4·12	Cg	vw	4·18	QGo		4·21	Q	s {	4·20
									Cg		4·07	Cg		4·07
														3·80
GCg	ms	3·69	GCg	vw	3·65	....	....	....	CgG	w	3·70	GCg	m {	3·68
QG	s	3·34	QG	w	3·34	QG	m	3·33	QG	s	3·34	QG	s	3·34
G	w(d)	3·08‡	G	vw	3·09	....	....	....	G	w	3·07‡	....	...	....
G	w	2·97	G	vw	2·95‖	....	....	....	GM	vw	2·97‖	....	....	....
G	w	2·84	..	. .	....	....	....	....	....	....	....	....	....	....
HGoG	vw	2·73	....	....	....	....	....	....	....	....	....	G(H)	?	2·69
G(M)	s	2·58	G(M)	s	2·58	G(M)	m	2·58	GM	m	2·57	GM		2·58
QGo		2·45	....	....	....	....	....	....	QGo	w	2·45	Q	m(d) {	
G	m {	§2·414	G	m(d)	2·409	G	w	2·394	....	....	....			2·444
Q		2·28	....	....	....	....	....	....	Q	vw	2·271	Q	w	2·275
G	vw {	§2·241	G	?	2·237	....	....	....	....	....	....	....	....	....
Q		2·22	. .	....	... .	Q	?	2·216	Q	vw	2·228	Q	w	2·212
GQ	vw	2·119	...	....	....	....	....	....	GQ	vw	2·119	GQ	w	2·120
GQ	vw	1·988	...	....	....	....	....	....	GQ	vw	1·975	GQ	w	1·970
U	?	1·887	....	....	....	....	....	....	....	....	....	U	vw	1·910
Q	m	1·814	....	....	....	....	....	....	Q	w	1·814	Q	m	1·814
U	vw	1·749	..	. .	....	....	....	....	....	....	....	....	....	....
G	w	1·710	G	vw(d)	1·715	....	....	....	GM	vw	1·700	GM	w(d) {	1·698
QG	m	1·659	QG	vw(d)	1·645	....	....	....	QG	vw	1·667	GQ		1·665
G	vw	1·608	....	....	....	....	....	....	....	....	....	....	....	....
G	vw	1·571	....	....	....	....	....	....	....	....	....	....	....	....
Q	w	1·538	....	....	....	....	....	....	Q	w	1·538	Q	m	1·538
G(M)	ms	1·510	G(M)	m	1·511	G(M)	w	1·505	GM	w	1·507	GM	vw	1·515
....	....		....	....		.. .	....		....	....		....	....	
QG	vw	1·451	QG	?	1·452	QG	vw	1·450	QG	vw	1·447	QG	vw	1·447
QG	vw	1·422	QG	?	1·415	. .	. .		QG	vw	1·409	..		
QG	m	1·376	QG	vw	1·372	....	. .		QG	w	1·374	QG	m	1·374
G	w	1·305	G	w {	1·303	G	vw	1·298	G	vw	1·307	G	vw	1·316
GQ	vw	1·288	GQ		1·283	...	..		GMQ	vw	1·288	GMQ	vw	1·288
QG	w	1·256	QG	vw	1·254	...	..		GMQ	vw	1·253	GMQ	w	1·257
QG	w	1·199	....	. . .		...	..		Q	?	1·227	Q	vw	1·227
Q	vw	1·181	....	....		....	..		QG	vw	1·196	QG	w	1·199
									Q	vw	1·180	Q	w	1·180

s = strong; ms = medium strong; m = medium; w = weak; vw = very weak; d = diffuse. G = Glauconite; Q = Quartz; M = Montmorillonite; K = Kaolinite; Go = Goethite; H = Haematite; Cg = Candle grease.

* Estimates of d/n made on films taken with Cu radiation.

† Centre of a line unsymmetrical in intensity which on its inner edge has a diffuse region extending to the line at 4.50 A and within this diffuse region a faint quartz line occurs at 4.26 A.

GREENSAND 61 μ AND LESS TAKEN WITH UNFILTERED Fe RADIATION, ALL OTHERS WITH RADIATION).

	Subsoil						Soil							
	2 μ and less.						61 μ and less.			2 μ and less.				
Possible Origin.	Unheated.		Possible Origin.	Heated 500°C.		Possible Origin.	Unheated.		Possible Origin.	Unheated.		Possible Origin.	Heated 500°C.	
	I.	d/n		I.	d/n		I.	d/n		I.	d/n		I.	d/n
M	m	15·4	....	....	....	....	..	....	....	....	....	....	..	....
(G)	?	9·27	M(G)	s	9·85	....	....	....	....	....	....	....	....	....
K	w	7·23	....	....	....	(K)	?	7·20	K	m	7·05	....	....	....
....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
(G)M	s {	4·48	(G)M	w	4·45	QGo/Cg {	w	4·20	KCg	m {	4·50	U	w	4·47
Cg	m {	4·14	Cg	s	4·10						4·12	Cg	vw	4·12‡
....	....	....	Cg	m	3·68	Cg	vw	3·70	....	....	....	Cg	?	3·65
K	w	3·55	....	....	....	....	....	....	K	w	3·55	....	....	....
Q(G)	w	3·33	Q(G)	m	3·33	Q	s	3·34	Q	s	3·33	Q	s	3·33
....	....	....	....	....	....	....	....	....	....	....	....	....	....	....
(H)(G)	?	2·67	H(G)	vw	2·68	HGo	vw	2·68	H	w	2·69	H	w	2·67
(G)M	m	2·58	(G)M H	vw {	2·58				K	m	2·57	....	....	....
....	....	....			2·485	H	w(d) {	2·51	KH	m	2·497	H	m	2·497
						QGo		2·44						
(G)	vw	2·418				....	....	....	K	vw	2·335	....	....	....
....	....	....				Q	vw	2·273	...	....	....	....	....	....
Q	w(d)	2·197	Q	w(d)	2·216	....	....	....	(Q?)	vw	2·189	(Q?)	vw	2·189
?Q(G)	w(d)	1·983	....	....	....	Q	vw	2·105	Q	vw	2·120	U	?	2·076
U	?	1·889	....	....	....	Q	vw	1·976	Q	vw	1·983	U	?	1·952
....	....	....	....	....	....	Q	m	1·814	Q	vw	1·814	QH	w(d)	1·824
(G)MQ	m(d)	1·683	....	....	....	Q	d	1·681	QK	vw(d)	1·672	QH	w(d)	1·688
....	....	....	....	....	....	U	vw(d)	1·606	U	vw	1·593	....	....	....
....	....	....	....	....	....	Q	m	1·538	Q	vw	1·538	....	....	....
M(G)	m(d) {	1·515	....	....	....	....	..	....	....	....	....	....	....	....
		....	M(G)	vw(d)	1·497	H	vw	1·488	K	w	1·490	..	....	....
		1·489				Q	vw	1·447	Q	w	1·452	....	....	....
...	....	....				....	..	....	(Q?)	vw	1·410	..	....	....
....	....	....				Q	m	1·374	Q	vw	1·373	..	..	....
(G)	w(d) {	1·305				....	....	....	....	....				
(G)MQ		1·283	...			Q	vw	1·284	...					
....			..			Q	vw	1·253	....					
....			..			Q	vw	1·226	....	...				
....			....			Q	vw	1·197	....			....	....	....
....			..			Q	vw	1·180	....			....	....	....

‡ Outer edge of a faint diffuse line that extends almost to the previous line.

§ Very faint spotted quartz lines occur on the inner edge of the line at 2.414 A and on the inner and outer edges of the line at 2.241 A.

⸗ This line has been considered as an (025) glauconite reflection.

In the case of the clay minerals the fact that they may be subdivided into three groups, each group being characterised by a particular large spacing, is made use of in their identification in soil colloids.

In preparing the following particulars regarding the chemical composition of members of the three groups of clay minerals the author has consulted Hendricks and Alexander (10).

(1) *Kaolinite Group.*—The kaolinite group includes the following minerals : kaolinite, anauxite, nacrite, dickite, halloysite and hydrous halloysite. These minerals, with the exception of hydrous halloysite which possesses two easily detachable molecules of water, have the ideal formula $[Al_2] [Si_2]O_5(OH)_4$ in which isomorphous replacement is largely restricted to mutual substitution of Al and Si in $[Si_2]$ positions. The characteristic large spacing for all members except hydrous halloysite occurs at approximately 7 A. Hydrous halloysite, which readily reverts to halloysite by the loss of two molecules of water, has a basal spacing of $10 \cdot 3$ A. The patterns of all members of this group are destroyed by heating to 500°C.

(2) *Montmorillonite Group.*—The montmorillonite group includes the following minerals : montmorillonite, saponite, nontronite and beidellite. Montmorillonite has the ideal formula $[Al_2] [Si_4]O_{10}(OH)_2.xH_2O$ in which extensive isomorphous replacement can take place. Substitution of $[Al_2]$ by $[Mg_3]$ gives saponite $[Mg_3] [Si_4]O_{10}(OH)_2.xH_2O$; substitution of $[Al_2]$ by $[Fe_2]$ gives nontronite $[Fe_2] [Si_4]O_{10}(OH)_2.xH_2O$; substitution of Si by Al in $[Si_4]$ position together with the replacement of O by (OH) or the replacement of Al in $[Al_2]$ position by other ions gives beidellite $[Al_2] [Si_3Al]O_9(OH)_3.xH_2O$ in which the $SiO_2 : (R_2O+RO)$ ratio lies close to 3 : 1. The characteristic large spacing for air dried material of all members occurs at 14–15 A. Members of this group show reversible lattice shrinkage and expansion according to their water content (11). Upon heating to 500°C. the 14–15 A basal spacing shrinks to 10 A.

(3) *Mica Group.*—In this group no subdivision is at present recognised. Gruner (12) however, has shown that the structures of glauconite and mica are almost identical. Mica has the ideal formula $K[Al_2] [Si_3Al]O_{10}(OH)_2$ in which extensive isomorphous replacement can take place. Replacement of K by H_2O accompanied by substitution of Si for Al in tetrahedral co-ordination or (OH) for O, together with Mg and Fe replacing $[Al_2]$ with octahedral co-ordination, results in a mineral of the glauconite type. The characteristic basal spacing for the mica group occurs at 10 A. No change in pattern is produced by heating members of this group to 500°C.

As the minerals within a group cannot readily be distinguished in the diffraction pattern of a soil colloid, the terms " kaolinite " and " montmorillonite " will be used, for brevity, in the remainder of this paper to designate a mineral belonging to the kaolinite group and montmorillonite group respectively.

In the drawing up of Table I. an attempt has been made to assign a possible origin to all the observed lines. For montmorillonite and kaolinite the data published by Kelley et al. (13) was used. This data includes only spacings to which Miller indices related to a definite unit cell could be assigned. The kaolinite spacings were those tabulated by Gruner (14) with respect to the monoclinic unit cell a = $5 \cdot 14$ A, b = $8 \cdot 90$ A, c = $14 \cdot 51$ A, β = 100° 12′. The montmorillonite spacings were selected from the data of Maegdefrau and Hofmann (15) who referred the mineral structure to an orthorhombic cell with dimensions a = $5 \cdot 18$ A, b = $8 \cdot 97$ A, with c variable according to the degree

of hydration.   The data relating to glauconite was taken from Gruner (12), who, by referring the mineral to the mica structure, was able to assign Miller indices to most of his recorded lines.

Quartz data was taken from Favejee (16) who has tabulated estimated interplanar spacings relating to the unit cell a = 4·903 A, c = 5·393 A.   Data supplied by Hanawalt, Rinn and Frevel (17) was used when considering the possibility of the presence of the oxides and hydroxides of Fe and Al.

In preparing Table I. the principle was employed of only assigning an origin to a line when on intensity considerations the line was likely to be contributed to by the mineral in question.

Considerable difficulty was encountered in recording 10 A diffraction lines because a pronounced central scattering extended out to about this spacing. Measurements of spacings in this region consequently vary considerably. Films taken with Cu radiation, however, often gave clear evidence of the existence of a 10 A line.

(1)   *Upper Greensand.*

The original observations of early workers on the high glauconite content of this sand have been confirmed.   A comparison between the fine and coarse fractions seems to indicate that there is a higher glauconite content in the coarse fraction.   The agreement between the glauconite spacings listed by Gruner and the spacings recorded for the coarse fraction of the upper greensand is sufficiently good to permit of a calculation of the unit cell dimensions of the Gingin glauconite assuming the mica structure of glauconite and the indices assigned by Gruner to the various spacings.   In this calculation the following lines and corresponding indices were used :   10·12 A (002) ;   2·58 A ($20\overline{2}$) ; 1·510 A (060) ;   1·305 A (400).

TABLE II.

UNIT CELL DIMENSIONS OF GLAUCONITE.

				Gingin glauconite.	Gruner's average of six samples.
c_0	...	...	...	20·21	20·03
b_0	...	...	...	9·06	9·07
a_0	...	...	...	5·24	5·24
β	...	...	...	94° 58′	95° 00′

Simpson (18) has noted the presence of dufrenite (a bright green basic ferric phosphate $Fe_2(OH)_3PO_4$) in the upper greensand but in the absence of any X-ray data, known to the author, with respect to this mineral and in the absence also of reasonably pure specimens from which X-ray data may be obtained, no conclusion has been reached as regards its presence in the sample examined in this study.   The presence of quartz has been previously referred to.

(2)   *Subsoil.*

The most noticeable differences between this pattern and the previous one are the existence of a 15 A and a 7 A spacing.   The 15 A spacing shrinks to 10 A and the 7 A spacing disappears when the sample is heated to 500°C.

These lines, it is considered, are the characteristic basal spacings of mont-morillonite and kaolinite. The 10 A glauconite spacing is greatly reduced in intensity. In comparing the two fractions of this sample it appears that the coarse contains more quartz and the fine contains more kaolinite.

(3) *Soil.*

In the coarse fraction quartz is the only constituent that can be definitely recognised. In the fine fraction however, in addition to the quartz pattern, there is a number of lines, including a 7 A line, which disappear when the sample is heated to 500°C. These lines, it is considered, are due to kaolinite. In both fractions there is a little haematite and/or goethite and a possible trace of glauconite.

Additional effects of Heat Treatment.

Several changes, in addition to those previously noted, occur in the X-ray patterns of the heat treated samples. In most unheated samples a broad area of strong intensity extends from 4·50–4·10 A, which after heat treatment, is resolved into two lines (4·5 and 4·1 A). In the greensand and soil samples the line with the larger spacing is the more intense whereas in the subsoil sample it is the less intense. The line with the smaller spacing is due to small amounts of candle grease which lined the walls of the celluloid containers in which the samples were mounted for X-ray analysis. The method employed for the preparation of celluloid containers using candle grease has been previously described (4). Candle grease is characterised by two strong lines which occur at 4·12 and 3·70 A and which far exceed in intensity any other lines in the candle grease pattern. It has been frequently noted that a line at 3·7 A either appears or is increased in intensity as a result of heat treatment. As the effect only appeared when kaolinite was present in the unheated sample it was suggested that the line could be due to a decomposition product of kao-linite (9). It is now believed that the appearance of this line at 3·7 A is not effected by heat treatment but is determined by the amount of candle grease present in the container. This is the origin of the 3·7 A line in the soil and subsoil samples.

It is also noteworthy that the characteristic quartz line at 3·34 A always increases or maintains its intensity after heat treatment.

MICROSCOPIC EXAMINATION.

A microscopic examination was undertaken with the object of determining whether or not the optical properties of the materials examined were consistent with the X-ray conclusions. Wherever possible refractive indices and bire-fringence were measured but because of the different stages of alteration present, particularly in the coarser fractions, the refractive indices in many cases are given only to the second place of decimals.

Throughout the work the samples were immersed in mixtures of clove oil and a − monochloronaphthalene for refractive indices up to 1·637, in mixtures of a − monochloronaphthalene and a − monobromonaphthalene for re-fractive indices between 1·637 and 1·661 and in mixtures of a − monobromona-naphthalene and methylene iodide for refractive indices higher than 1·661. The indices were determined in sodium light by means of a Pulfrich refracto-meter.

The Coarse Fractions.

Upper Greensand.—This sample contains an amount of crystalline material intermediate between the amounts occurring in the soil and subsoil. The main constituent minerals are glauconite and quartz. The glauconite occurs in yellow-green to brown non-pleochroic grains which show aggregate polarisation. The refractive indices lie between 1·600 and 1·620. This gives a maximum birefringence of 0·020. The quartz content is not high. The grains are subangular and are usually coated with glauconite granules.

There occurs in addition to glauconite and quartz a small amount of each of the following particles :—

(a) A light green fibrous mineral which in its clear unaltered form has a refractive index greater than, but close to, methylene iodide (1·74). The birefringence is variable but not high. The fibres, which have positive elongation are always arranged in a radial manner, giving a spherulitic structure. The fibres when viewed end on are greenish-blue, non-pleochroic, with the birefringence masked by the original colour. In this orientation the mineral is granular in appearance, frequently coats other minerals and has a range of refractive indices from about 1·68—1·72.

Alteration readily takes place at the periphery of the spherulites, sectors of which then show a plumose structure. The alteration is accompanied by a reduction in refractive index and an increase in birefringence. As alteration advances the fibrous structure is lost and the grains take on an oolitic appearance (in the form of concentric shells) while still retaining the spherulitic cross. These grains are markedly birefringent and the refractive indices lie between 1·66 and 1·685. At this stage the grains tend to break up into smaller curved laminae formed by the splitting off of successive concentric shells. In these particles the refractive index is decreased but does not drop below about 1·58. The birefringence is also often decreased.

(b) Brownish-coloured grains, some of which show traces of a spherulitic cross. The birefringence of these particles is obscured by the colour, but the refractive indices vary from 1·61—1·64.

(c) Particles very similar to the alteration products of (a) but distinguished from them by the absence of a spherulitic cross. The particles are only of weak to moderate birefringence and the mean refractive index is about 1·585. The low birefringence could be due to lack of orientation of aggregating particles, but an occasional particle is sufficiently well oriented to give a biaxial figure of negative optical character and of small axial angle.

(d) Particles distinguished from (c) merely by the fact that they are only very weakly birefringent and their refractive indices vary from 1·535—1·555. Their colour is light yellow-green.

The Subsoil.—The most noticeable feature of the subsoil is the large amount of crystalline material of which only a small amount is quartz and glauconite. The quartz as before forms subangular grains coated with other minerals. The glauconite is recognised by its possessing similar optical properties to the glauconite in the upper greensand. The refractive indices are, however, a little lower. the range being from 1·58—1·60. The remainder of the sample is made up of the particles a—d considered in the upper greensand section.

The Soil. The most noticeable feature of the soil sample is the small amount of crystalline material of which quartz is the main constituent. This mineral is heavily coated with iron oxides. Occasional grains of glauconite and the alteration products previously described (of which some of the brown grains show traces of a spherulitic cross) occur but the main fraction of the sample consists of opaque grains yellow-brown in reflected light. Reddish-brown iron oxide grains are frequent.

The Fine Fractions.

In the determination of the optical properties of the 2 μ fractions use was made of the fact (19) that individual particles existing in a soil colloid suspension tend to orient themselves after drying into aggregates which possess uniform optical properties. This takes place even when two or more clay minerals are present so that the optical properties of the aggregates depend upon the proportion of the different constituents forming the aggregates.

In the soil colloids examined in this study there was no marked tendency for the aggregates to show a crystallographic orientation of the individual particles. No aggregates were found sufficiently well oriented to give an interference figure from which the optical character could be determined. However, enough oriented aggregates were found to determine the optical constants.

The upper greensand fraction when viewed beneath the microscope was seen to be in the form of light green aggregates up to 50 μ and greater in diameter. About 25 per cent. of these aggregates show fairly uniform crystallographic orientation of individual components and for these $\gamma - \alpha = 0 \cdot 01$. The remainder of the aggregates are non-birefringent.

The subsoil fraction when viewed beneath the microscope was seen to be in the form of light yellowish-brown aggregates up to 50 μ and greater in diameter. There is about the same proportion of birefringent material as in the upper greensand sample. The birefringence as measured appears to be about $0 \cdot 005$. This figure is probably low due to the fact that the colloid particles are probably coated with iron oxides or hydroxides which obscure the birefringence.

The soil fraction when viewed beneath the microscope was seen to be in the form of dark brown non-birefringent particles up to 50 μ and greater in diameter.

The optical properties of aggregates of the soil colloid fractions from the upper greensand, subsoil, and soil are summarised in Table III.

TABLE III.

OPTICAL DATA RELATING TO THE FINE FRACTIONS.

Sample.	α $\pm 0 \cdot 002$	Mean Refractive Index $\pm 0 \cdot 005$	γ $\pm 0 \cdot 002$	$\gamma - \alpha$
Upper greensand	1·618	...	1·628	0·010
Subsoil	1·600	...	1·605	0·005
Soil	...	1·620	...	...

DISCUSSION.

Coarse Fractions.—X-ray evidence indicates that in the coarse fractions the glauconite content decreases and the quartz content increases in passing from greensand to soil.   The microscopic examination confirms this.   X-ray evidence also indicates the presence of montmorillonite and a little kaolinite in the subsoil, a possible trace of montmorillonite in the greensand and of kaolinite in the soil.   In view of the fact that the samples examined contain a fibrous mineral with spherulitic structure which has not been identified and which readily alters in a characteristic manner to give a variety of particles some of which have optical properties similar to clay minerals it has not been possible to verify beneath the microscope the presence of any clay minerals in these fractions.

Fine Fractions.—For the fine fractions X-ray evidence indicates that glauconite is the main constituent of the upper greensand, montmorillonite the main constituent of the subsoil, and kaolinite the main constituent of the soil.   Optical data relating to pure clay minerals have been summarised by the author elsewhere (19).   Members of the montmorillonite and mica groups have similar optical properties which are markedly different from the optical properties of members of the kaolinite group.   In Table III. it is seen that the upper greensand and subsoil have similar optical properties, both samples being more birefringent than the soil sample which is non-birefringent.   The non-birefringent character of the soil sample could be due to the presence of kaolinite or to the presence of coatings of iron oxides or hydroxides on the soil colloid particles which tend to mask the birefringence. It is believed that both play a part.   It must be realised that the optical properties of aggregates of the fine fractions depend on all the constituents present, so that only broad generalisations may be drawn when the main constituents alone are considered.   Generally speaking the optical properties of the fine fractions are consistent with the composition as determined by X-ray analysis.

CONCLUSIONS.

With regard to the composition of the samples X-ray data lead to the conclusions summarised in Table IV.   Some modifications, the extent of which it is difficult to estimate, may be necessary in the light of the following considerations :—

(a) The relation between relative intensities of lines and relative quantity of corresponding diffracting material.   All estimates of relative quantities of the different constituents are based on visual observation of line intensities.   These estimated relative quantities may correctly indicate the actual relative quantities only if the ratio of the intensities of patterns of different constituents is equal to the ratio of the proportions of the constituents.   This may not be true and may depart widely from the truth if quartz is one of the constituents since the diffracting power of quartz is markedly greater than that of any clay mineral (9).

(b) Microscopic evidence.

From Table IV. the following generalisations as regards mineral changes in passing from greensand to soil may be drawn :—

(a) The content of glauconite decreases.

(b) The content of kaolinite, quartz and oxides and hydroxides of iron increases.

(c) The montmorillonite content is concentrated in the subsoil.

It is hence suggested that in the weathering of glauconitic greensand the glauconite alters firstly to a clay of the montmorillonite group which later is replaced by a clay of the kaolinite group together with free quartz and haematite and/or goethite. The formation of kaolinite through the splitting off of silica from montmorillonite has been suggested by Kelley et al. (13) as an explanation of the occurrence of kaolinite clay overlying montmorillonite clay in the Susquehanna soil colloids.

It is quite logical to expect on this hypothesis that kaolinite would be present with montmorillonite in the subsoil fraction but it must also be borne in mind that contamination of the subsoil fraction with the overlying soil would give kaolinite in the subsoil fraction. Such a contamination of the subsoil fraction is considered to be negligible.

TABLE IV.

COMPOSITION OF THE THREE SAMPLES.

(From X-ray evidence only).

Mineral.	Upper Greensand.		Subsoil.		Soil.	
	Coarse.	Fine.	Coarse.	Fine.	Coarse.	Fine.
Glauconite ...	Very much	Much	Little	Little	Possible trace	Possible trace
Quartz	Little	Very little	Much	Very little	Very much	Little
Montmorillonite ...	Possible trace	Possible trace	Much	Much	...	...
Kaolinite ...	...	...	Little ⟶ Little		Possible trace	Much
Haematite and/or Goethite	Very little	...	...	Possible trace	Little	Little

Note.—An arrow (⟶) indicates an increasing amount of kaolinite.

ACKNOWLEDGMENTS.

The author wishes to express his thanks to the University of Western Australia Text Books Board and to the authors of " Junior Geology " for permission to reproduce Fig. I. To the Text Books Board the author is also very greatful for the loan of the block of this figure. To Miss M. Bowen the author's thanks are due for the drawing of Fig. 2.

BIBLIOGRAPHY.

(1) Glinka, K. : " Der Glaukonit, seine Enstehung, sein chemischer Bestand und seine Verwitterung," Saint-Pétersbourg, 1896, p. 114.

(2) Cayeux, L. : " Les Roches Sedimentaires, Paris," 1916.

(3) Denison, I. A., Fry, W. H., and Gile, P. L. : " Alteration of Muscovite and Biotite in the Soil." U.S. Dept. of Agric. Tech. Bull. 128, 1929.

(4) Shearer, J., and Cole. W. F. : " Analysis of Soil Colloids by X-ray Diffraction Methods." Jour. Roy. Soc. W. Aust. 1939–40, XXVI., pp. 121–131.

(5) Clarke, E. de C., and Hanrahan, L. F. : " Junior Geology," Perth, 1941.

(6) Feldtmann, F. R. : " The Glauconite Deposits at Gingin, South-West Division." Ann. Prog. Rept. Geol. Surv. West. Aust. 1933, p. 6.

(7) Hosking, J., and Greaves, G. A. : " A Soil Survey of an area at Gingin, Western Australia." Jour. Roy. Soc. W. Aust. 1935–36, XXII., pp. 71–112.

(8) Wood, W. A. : " Note on the elimination of the β wave length from the characteristic radiation of iron." Proc. Physic. Soc. 1931, 43, pp. 275–278.

(9) Shearer, J., and Cole. W. F. : " X-ray analysis of some Tasmanian Soil Colloids." Jour. Roy. Soc. W. Aust. 1939–40, XXVI., pp. 133–137.

(10) Hendricks, S. B., and Alexander, L. T. : " Minerals present in Soil Colloids : I. Description and Methods for Identification." Soil Sci. 1939, 48, pp. 257–267.

(11) Hofmann, U., Endel, K., and Wilm, D. : " Kristallstruktur und quellung von Montmorillonit." Zeit. f. Krist. 1935, 86, p. 340.

(12) Gruner, J. W. : " The Structural Relationships of Glauconite and Mica." Amer. Min. 1935, 20, p. 699.

(13) Kelley, W. P., Woodford, A. O., Dore, W. H., and Brown, S. M. : " Comparative Study of the Colloids of a Cecil and a Susquehanna Soil Profile." Soil Sci. 1939, 47, pp. 175–193.

(14) Gruner, J. W. : " Crystal Structure of Kaolinite." Zeit. f. Krist. 1932, 83, pp. 75–88.

(15) Maegdefrau, E., and Hofmann, U. : " Die Kristallstruktur des Montmorillonits." Zeit. f. Krist. 1937, 98, pp. 299–323.

(16) Favejee, J. Ch. L. : " Zur Methodik der Rontgenographischen Boden-forschung." Zeit. f. Krist. 1939, 100, p. 425.

(17) Hanawalt, J. D., Rinn, H. W., and Frevel, L. K. : " Chemical Analysis by X-ray Diffraction." Ind. & Eng. Chem., Anal. Ed. 1938, 10, pp. 457–512.

(18) Simpson, E. S. : " Contribution to the Mineralogy of Western Australia." Jour. Roy. Soc. W. Aust. 1936–37, XXIII, pp. 17–35.

(19) Cole, W. F. : " Results of a Microscopic Study of some Soil Colloids." Jour. Roy. Soc. W. Aust. 1940–41, XXVII., pp. 1–7.